

ELECTROCHEMICAL BEHAVIOR OF CHROMIUM (II) AND CHROMIUM (III)
IONS ON A MERCURY DROP ELECTRODE IN SULFATE MEDIA

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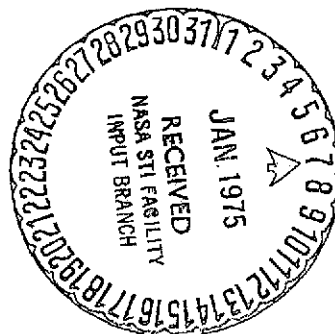
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16. Abstract The transport numbers, Cr (II) \rightarrow Cr (III) oxidation-reduction reaction exchange currents, and composition and apparent instability constants of the Cr (III) sulfate complexes formed were determined. An unusual temperature dependence of the Cr (II)-Cr (III) ion reduction-oxidation reactions was found in dilute (0.1 M and lower) solutions, which passed through a maximum. This is explained by a change in Cr (III) complex compositions in the solution.					
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ELECTROCHEMICAL BEHAVIOR OF CHROMIUM (II) AND CHROMIUM (III)
IONS ON A MERCURY DROP ELECTRODE IN SULFATE MEDIA

P.I. Zabotin, Ye.I. Vasil'yeva, V.M. Tsokalo and G.Z. Kir'yakov

In electrodeposition of chromium on solid or mercury electrodes, and in corrosion of chromium and its alloys, the Cr (II), Cr (III) oxidation-reduction reaction takes place. The reaction $\text{Cr (III)} \rightleftharpoons \text{Cr (II)}$ can also characterize the specifics of the effect of the nature and composition of the solution on many electrode processes, taking place with chromium ions. /52*

Trivalent chromium may be in a sulfuric acid medium (according to Werner [1]), both in the form of the hexahydrate $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (violet modification), and in the form of a complex, in which part of the water is replaced by the sulfuric acid anion (green modification). A.V. Pamfilov and A.I. Lopushanskaya and colleagues [2-6], studying the behavior of Cr (III) in nitrate, chloride and sulfate solutions, polarographically, spectrophotometrically and galvanostatically, think that the green modification of chromium is not a product of replacement of water in the inner sphere of the complex trivalent chromium ion by the acid anion, but is a product, formed as a result of polymerization of a hydroxo or oxo compound of trivalent chromium.

The existence of polymer molecules of trivalent chromium, connected by means of hydroxyl ($-\text{OH}-$) bridges or oxo ($-\text{O}-$) bridges, a portion of which may also be replaced by Cl^- , SO_4^{--} and others, also is noted in works [7-10]. In this case, the hydroxylation and oxolation processes favor an increase in temperature and alkalinity of the solution. Moreover, compounds of the type $[\text{Cr}(\text{H}_2\text{O})_y\text{Ax}]^{2\pm}$ are known, which do not contain hydroxo groups, and where A are various complex-forming groups [10, 11].

* Numbers in the margin indicate pagination in the foreign text.

Arđon and Linenberg have observed that, in oxidation of divalent chromium by acid in a perchlorate medium, binuclear Cr (III) complexes form, with an oxo or a hydroxo bridge. Thus, it is evident that, depending on composition of the medium and other conditions, various types of complex Cr (III), Cr (II) compounds may occur, with one competing group or another (H_2O , NH_3 , amines, OH^- , various anions, etc.) or mixtures of them.

We have attempted in this work to give the principal attention to the effect of sulfate anion concentration on the electrochemical behavior of the Cr (II) and Cr (III) ions in water solutions. Since it is well-known [13] that, in sulfate media, trivalent chromium produces irreversible reduction waves, for evaluation of certain kinetic parameters of the Cr (II) - Cr (III) oxidation-reduction reaction, and for evaluation of the fractional participation of sulfate anions in formation of the chromium complexes in sulfate media, analysis of the anode-cathode irreversible polarographic waves of A.G. Stromberg was used [14-18].

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Polarography was carried out mainly by the method described earlier [19], using Lp 55 and Lp 60 polarographs.

A solution containing Cr (II) was prepared by electrolysis of trivalent chromium sulfate (~ 10 g/l Cr), in a separate sealed electrolyzer, with the anode and cathode compartments separated by a porous glass diaphragm. The electrolysis conditions: cathode, lead; anode, platinum; cathode current density $100-200$ A/m² ($10^{-2}-2 \cdot 10^{-2}$ A/cm²); electrolysis time, 3-4 hours, bulk current density 5-15 A/l. The electrolysis was carried out, until accumulation of $\sim 50\%$ of the total chromium content as Cr (II) in the solution. Analysis of divalent chromium was carried out by the well-known iodometric method. The total chromium content in the final solution for polarography was $3-4 \cdot 10^{-3}$ M. Galvanometer sensitivity with the working shunt (1/200) was $5.6 \cdot 10^{-7}$ A/mm. The quantities m and τ , characterizing

the properties of the capillary at $\phi = -1.0$ V in the polarograph solution, were $m = 2.45 \text{ mg} \cdot \text{sec}^{-1}$ and $\tau = 3.6 \text{ sec}$, respectively.

Experimental Section

Polarograms of reduction of Cr (III) (curves K) and oxidation of Cr (II) (curves A), in a mercury drop electrode, on a background of 0.01, 0.1, 0.5 and 1.0 M Na_2SO_4 [$(\text{NH}_4)_2\text{SO}_4$], with solution pH 2.9-3.7, are presented in Fig. 1.

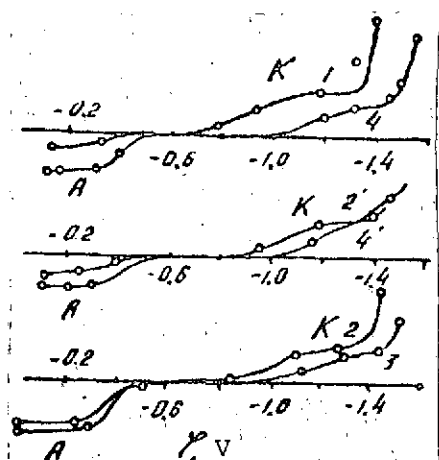


Fig. 1. Polarograms of Cr (III) reduction (K) and Cr (II) oxidation (A), in mercury drop electrode, on background of 0.01-1 M SO_4^{2-} solutions, t 25°; 1. 0.01 M Na_2SO_4 , pH 3.1; 2. 0.1 M Na_2SO_4 , pH 3.3; 2'. 0.1 M Na_2SO_4 , pH 2.9; 3. 0.5 M Na_2SO_4 , pH 3.7; 4. 1.0 M $(\text{NH}_4)_2\text{SO}_4$, pH 3.4; 4'. 1.0 M $(\text{NH}_4)_2\text{SO}_4$, pH 3.2.

in the complex Cr (III) compounds, discharged at the cathode, the equation of A.G. Stromberg was used [14-17]. In this case, the exchange current calculations were carried out by a

The curves in Fig. 2 express $\log \frac{i}{i_d - i}$ for the anode (A) and cathode (K) waves of Cr (II) \leftrightarrow Cr (III), vs. cathode potential.

The anode and cathode half-wave potentials were determined more precisely from the curves of Fig. 2. The slope angles b/α and b/β and the transport numbers t_{α} and t_{β} were determined from them also.

For calculations of the equilibrium potentials of the Cr (III)-Cr (II) half-waves, the exchanger currents or exchange current densities of this oxidation-reduction reaction, as well as the coordination number of site P, occupied by the SO_4^{2-} anions

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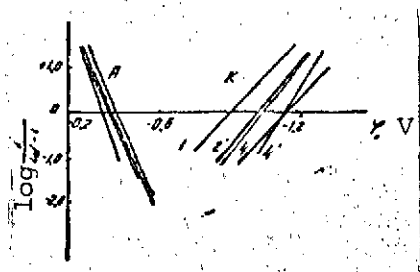


Fig. 2. $\log \frac{1}{i_d - i}$ vs. ϕ
for Fig. 1 polarograms;
designations the same.

formula, taking the inequality of the sum of coefficients $\alpha + \beta$ to one into account

$$\log i_0 = \frac{\alpha}{\alpha + \beta} \log I_a + \frac{\beta}{\alpha + \beta} \log I_k - \frac{\alpha \cdot \beta}{(\alpha + \beta)} b \Delta \varphi_{1/2} a^{-k} \quad (1)$$

The equilibrium potential of the Cr (III)-Cr (II) oxidation-reduction on the mercury drop electrode was calculated from equation (2) also considering that $\alpha + \beta \neq 1$

$$\varphi_p = \frac{\alpha}{\alpha + \beta} \varphi_{1/2}^k + \frac{\beta}{\alpha + \beta} \varphi_{1/2}^a + b \log \frac{I_k}{I_a} \quad (2)$$

The dependence of the half-wave potentials of the irreversible Cr (III) reduction, Cr (II) oxidation waves and the Cr (III) \rightleftharpoons Cr (II) oxidation-reduction reaction vs. the logarithm of the SO_4^{2-} addend-anion concentration ($\phi_{1/2} - \log C_x$) is presented in Fig. 3, and the dependence of the transport numbers α and β and exchange current density ($i_0 \text{ AA} \cdot \text{cm}^{-2}$) of the Cr (III) \rightleftharpoons Cr (II) reaction on the drop electrode in sulfate solution vs. logarithm of the SO_4^{2-} anion concentration (C_x) is depicted in Fig. 4.

It follows from Fig. 4 that the Cr (III)-Cr (II) oxidation-reduction reaction takes place in sulfate solutions, at quite a low rate, which is indicated by the low values of the exchange current densities. The equilibrium potential of this reaction and the exchange points depend heavily on the sulfate anion concentration in the solution, which is confirmed by the reaction of Cr (III) with SO_4^{2-} anions. The dependences of $\phi_{1/2}$ and i_0 on $\log C_x$, represented in the graphs, permits a quantitative

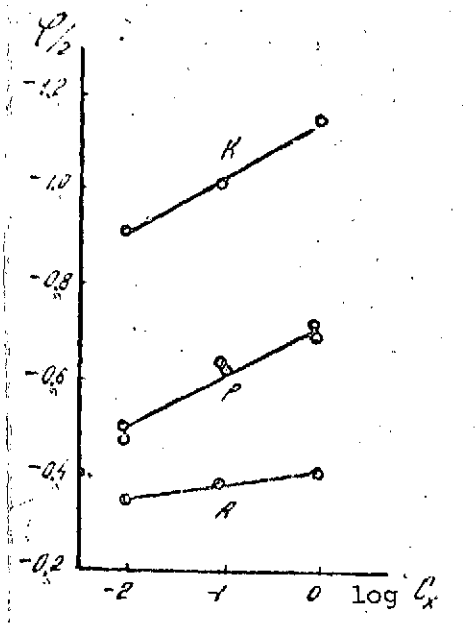


Fig. 3. Half-wave potentials of Cr (III) reduction (K), Cr (II) oxidation (A) and equilibrium potential of $\phi_{1/2}$ P half-wave of Cr (II)-Cr(III) oxidation-reduction (P) vs. \log concentration SO_4^{2-} .

estimate of certain properties of the Cr (III) complexes formed and discharged.

Data on the dependence of the Cr (III)-Cr (II) reduction-oxidation half-wave potentials and the equilibrium potentials of the reaction vs. the logarithm of the SO_4^{2-} anion concentration, in sulfate-perchlorate solutions, with a total $\text{Na}_2\text{SO}_4 + \text{NaClO}_4$ content = 1 M, are presented in Fig. 5. The perchlorate anion was used, as the most inert, from the point of view of complex formation of the additive, to maintain a constant ion strength.

The dependence of the Cr (III) \rightleftharpoons Cr(II) exchange reaction current density i_0 vs. the logarithm of the sulfate anion concentration ($\log C_x$), in a solution containing 1 M $\text{Na}_2\text{SO}_4 + \text{NaClO}_4$ is shown in Fig. 6.

In tests with perchlorate-sulfate solutions, a larger spread of the experimental points was observed than in pure sulfate solutions. This is especially evident from Fig. 6, in which the values of the Cr (III) \rightleftharpoons Cr (II) exchange reaction current densities are presented, with various SO_4^{2-} concentrations in the solution.

The deterioration in reproducibility most likely is connected with the fact that, in tests with the perchlorate-sulfate

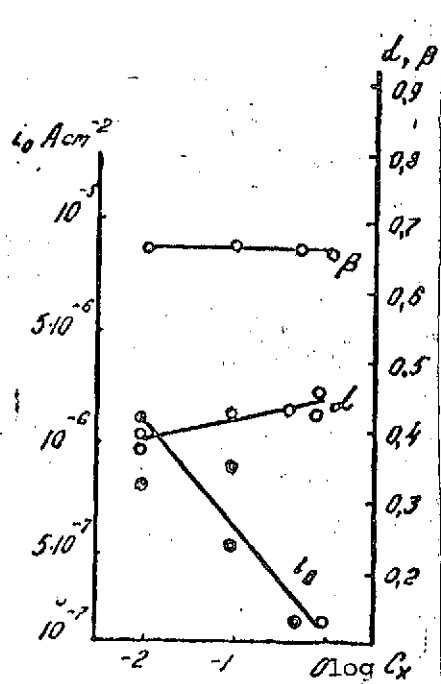


Fig. 4. Transport numbers α and β and exchange current density i_0 of Cr(III)-Cr(II) reaction vs. \log concentration Na_2SO_4 ($\log C_x$), pH 2.9-3.4, t 25°, $\text{Cr}_{\text{total}} = 3-4 \cdot 10^{-3}$ M.

solutions, greater variations in the solution pH was permitted, than in the tests with sulfate solutions. A common cause of some spread in the experimental points, for some solutions and others, most likely is the slowness of transformation of some complexes into others, before establishment of complete equilibrium and the impossibility of arbitrarily increasing the time for preliminary stabilization of the solutions, because of decomposition of the divalent chromium in the solutions.

Despite some spread of points in Fig. 6, it can, however, be stated that the Cr(III) \rightleftharpoons Cr(II) exchange current densities at 25° and in sulfate-perchlorate solutions remain low. Within a

certain tolerance, it also can be assumed that the exchange current density i_0 , for Cr(III)-Cr(II) in perchlorate-sulfate solutions, changes negligibly on the average with the logarithm of the SO_4^{2-} anion concentration (average value is $\sim 10^{-6}$ A/cm²).

It is evident from Fig. 5 that the equilibrium potentials of the Cr(III)-Cr(II) oxidation-reduction reaction half-waves in the perchlorate-sulfate solutions, also changes with the logarithm of the SO_4^{2-} concentrations, but to a lesser extent, than in pure sulfate solutions. This noticeable difference in behavior of Cr(III) and Cr(II), with identical changes in SO_4^{2-} concentration in sulfate and sulfate-perchlorate solutions, may

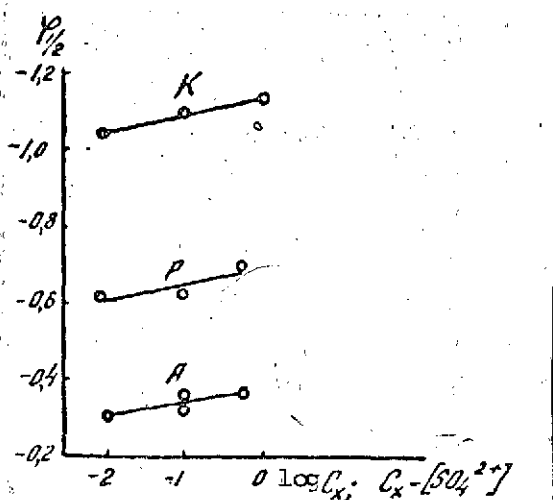


Fig. 5. Half-wave potentials $\phi_{1/2}$ of Cr (III) reduction (K), Cr (II) oxidation (A) and the equilibrium half-wave potential $\phi_{1/2}$ of the Cr (III) + Cr (II) oxidation-reduction vs. log concentration SO_4^{2-} ($\text{Na}_2\text{SO}_4 + \text{NaClO}_4 = 1 \text{ M}$, $t = 25^\circ$).

indicate that the ClO_4^- anions are not completely indifferent to Cr (III). Thus, the change in equilibrium half-wave potentials of the Cr (III) \rightleftharpoons Cr (II) oxidation-reduction reaction with change in SO_4^{2-} concentration (with $[\text{SO}_4^{2-}] + [\text{ClO}_4^-] = 1 \text{ M}$), may reflect a change from predominance in the solution of hydrate and chlorate Cr (III) complexes to sulfate. It is evident that the latter are more stable, since $\phi_{1/2p}$ shifts more in the negative direction with increase in SO_4^{2-} concentration, than with increase in ClO_4^- concentration.

These conclusions are in conformance with the thought of F. Rozotti [1, p. 13], who noted: "It usually is erroneously assumed that sodium perchlorate is used as the ionic medium, because the perchlorate ion does not form complexes. Hg (I), Fe (III), and Ce (III) at least form perchlorate complexes."

According to the equation

$$\begin{aligned} \varphi_{1/2 \text{ comp}} - \varphi_p = & \frac{RT}{2(n-m)F} \log \frac{D_{\text{Red}}}{D_{\text{Ox}}} - \frac{RT}{(n-m)F} \log \frac{K_{\text{Ox}}}{K_{\text{Red}}} - \\ & - (p-q) \frac{RT}{(n-m)F} \log [x], \end{aligned} \quad (3)$$

the values of $K_{\text{Ox}}/K_{\text{Red}}$, the ratio of the stability constant of trivalent chromium complexes to the stability constants of

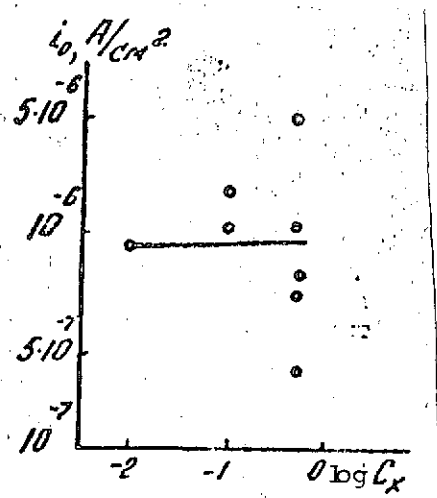


Fig. 6. Cr (III) \rightleftharpoons Cr (II) exchange reaction current density i_0 vs. $\log \text{SO}_4^{2-}$ concentration ($\log C_x$) in ($\text{Na}_2\text{SO}_4 + \text{NaClO}_4 = 1 \text{ M}$, pH 1.8-3.7, $t = 25^\circ$) solution.

divalent chromium complexes, as well as the values of $(p - q)$, the difference in ligand numbers of both complexes, were calculated. If it is assumed that divalent chromium ions occur mainly in the form of hexahydrates, i.e. $K_{\text{red}} \sim 1$, the value of $K_{\text{ox}}/K_{\text{red}}$ will determine the stability constant of trivalent chromium K_{ox} , and the value of $(p - q)$, the value of p' , the number of coordination sites, substituted in the six-water complex of trivalent chromium. It also was assumed in the calculations that ϕ_p , the equilibrium potentials of the oxidation-reduction half-wave of the Cr (III) and Cr (II) hexahydrates, can be determined from equation (2). /57

The accuracy in determination of the stability constants (or instability K) depends on the degree of approximation of the assumed values to the actual ones.

For the case of Cr (III) complex formation in sulfate solutions of 0.01, 0.1 and 1.0 M Na_2SO_4 at 25° (see Fig. 3),

$$\frac{\Delta(\phi_{1/2})_p}{\Delta \log C_x} = b \cdot p = 0.059 p; \Delta(\phi_{1/2})_p = 0.059 \log K' - 0.059 p \log C_x.$$

For the section of the curve from -2 to 0: $p \sim 2$, $K' = 2.7 \cdot 10^{-4}$. For solutions with a total concentration of $\text{Na}_2\text{SO}_4 + \text{NaClO}_4 = 1 \text{ M}$, $t = 25^\circ$ (Fig. 5): $p \sim 2$; $K_2' = 1.1 \cdot 10^{-2}$.

The composition of the discharged complexes can be estimated, by using the equation of A.G. Stromberg, on the basis of which the concept of Gerisher was proposed, on the connection between

the composition of the discharged complexes and the dependence of current density on concentration of the complex-forming reagent

$$\frac{\partial \lg i_0}{\partial \lg C_x} = P_2 + \frac{\beta}{b} \frac{\partial \varphi_p}{\partial \lg C_x}, \quad (4)$$

where P_2 is the composition of the complexes discharged at the cathode.

Since

$$\frac{\partial \varphi_p}{\partial \lg C_x} = -bP_1,$$

where P_1 is the composition of the complex predominating in the solution,

$$\frac{\partial \lg i_0}{\partial \lg C_x} = P_2 - \beta P_1.$$

In accordance with Fig. 3,

$$\frac{\partial \lg i_0}{\partial \lg C_x} = 0,665 = P_2 - \beta P_1,$$

where $P_1 = 1.2$.

If the value of β is assumed to be 0.006, $P_2 \sim 2$.

In this manner, by an approximate estimate, the composition of the discharged Cr (III) complexes in sulfate media is close to the composition of the complexes occurring in the solution in the predominating quantity, and the sulfate group in them occupies two coordination sites.

Interesting singularities of the electrochemical behavior of the Cr (III)-Cr (II) ions in sulfate media are displayed with

change in solution temperature. The nature of the dependence of Cr (III) \leftrightarrow Cr (II) exchange current densities in 0.1 M Na₂SO₄ on temperature, obtained for five series of solutions, with pH from 1.7 to 3.0, are shown in Fig. 7. The trend of this dependence is unusual; the temperature does not affect the oxidation-reduction reaction exchange current in the 30-70° range. However, if the nature of the curves of the four series of tests is taken into consideration from the fifth one, some increase in exchange current can be noted in the temperature region around 50° and, again, some decrease in them with increase in temperature to 70°.

A.V. Pamfilov et al. [2-6] has already noted a change in certain properties of chromium salts in water solutions, in the transition through the solution temperature around 40°, which was explained by change in structure of the water at this temperature. This phenomenon has been confirmed by our example of change in reaction exchange current densities in 0.1 M sulfate solutions. /58
 However, in more concentrated SO₄²⁻ solutions, we did not observe similar facts. Evidently, the properties of the chromium ions do not change in all cases, with change in water structure. How are Cr (III) solutions described, with respect to low SO₄²⁻ concentrations? The smaller the SO₄²⁻ excess in the solution, the lower its temperature and, apparently, the lower the concentration of OH⁻ ions, the less the competitive capacity of the SO₄²⁻ and OH⁻ groups, compared with water molecules, in formation of complex compounds with Cr (III) and the more likely the preferred formation in the solution of the chromium hexahydrate ion [Cr(H₂O)₆]³⁺. With increase in temperature of these solutions, the exchange current changes, as a result of two factors. On the one hand, the increase in temperature, as usual, decreases the extent of irreversibility of the processes. On the other hand, with increase in temperature, the violet modification of the chromium ion changes to green, i.e. the equilibrium between the hydrated chromium ions and sulfate or hydroxysulfate Cr (III) complexes of the [Cr(H₂O)₆] - x - y · (SO₄)_x(OH)_y ^(3 - 2x - y) type,

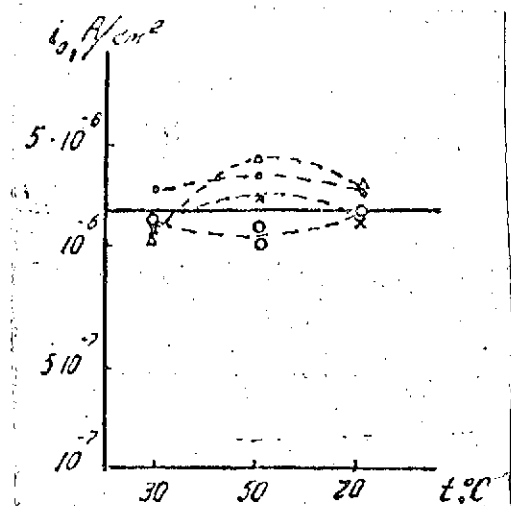


Fig. 7. $\text{Cr}(\text{III}) \rightleftharpoons \text{Cr}(\text{II})$ reaction exchange current density i_0 in 0.1 M Na_2SO_4 vs. temperature, for five series of solutions, pH 1.7-3.0.

shifts in the direction of formation of the latter. At identical temperatures, the green salts are characterized by lower exchange current densities for the reaction indicated above than the violet trivalent chromium hexahydrate. In more concentrated SO_4^{2-} solutions, the temperature effect is imperceptible, because, with an excess of SO_4^{2-} , the equilibrium between purely hydrated $\text{Cr}(\text{III})$ ions and sulfate complexes is shifted in the direction of formation of the sulfate form at still lower temperatures. With increase in temperature, the reversibility of the $\text{Cr}(\text{III})$ -

$\text{Cr}(\text{II})$ oxidation-reduction reaction usually increases, for monotypic complexes.

For precise definition of the effect of temperature on the $\text{Cr}(\text{III})$ - $\text{Cr}(\text{II})$ oxidation-reduction exchange currents in sulfate solutions with low SO_4^{2-} concentrations, a special polarographic study was carried out. In this case, to improve standardization of the polarography conditions assigned, a method was worked out for obtaining the sulfate salt of divalent chromium in crystal form. Solutions containing $\text{Cr}(\text{III})$ - $\text{Cr}(\text{II})$ were prepared from the salt obtained, without heating (at 20°), for the purpose of establishing a constant composition of the chromium complexes and improvement in reproducibility of the tests. The preparation, storage, and polarography of the solutions were accomplished in a hydrogen atmosphere. Heating and cooling of them for study of the effect of temperature was carried out right in the polarographic cell, by means of a thermostat. The drop electrode potential was

measured by the compensation method. A type Lp 60 polarograph, with an automatic electronic recorder, was used for the study. The total chromium content in the polarography solution was $3.85 \cdot 10^{-3}$ M. The sensitivity of the electronic galvanometer, with 1/300 and 1/500 shunts, was $3 \cdot 10^{-7}$ and $5 \cdot 10^{-7}$ A/mm, respectively. The capillary characteristics: -3.6 sec (at -1.0 V); m is $1.789 \text{ mg} \cdot \text{sec}^{-1}$.

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In study of the effect of temperature on the polarographic behavior of the Cr (III)-Cr (II) ions, each "temperature point" was investigated twice. The first time, with the prepared solu-

tion heated initially, and the second time, with cold solution. This procedure resulted in discovery of the non-equilibrium nature of the system in one case or another, which must have been manifested in noncoincidence of the results of polarography of the solutions for the "forward" and "reverse" directions of temperature change. The appearance of several polarograms is shown in Fig. 8-10.

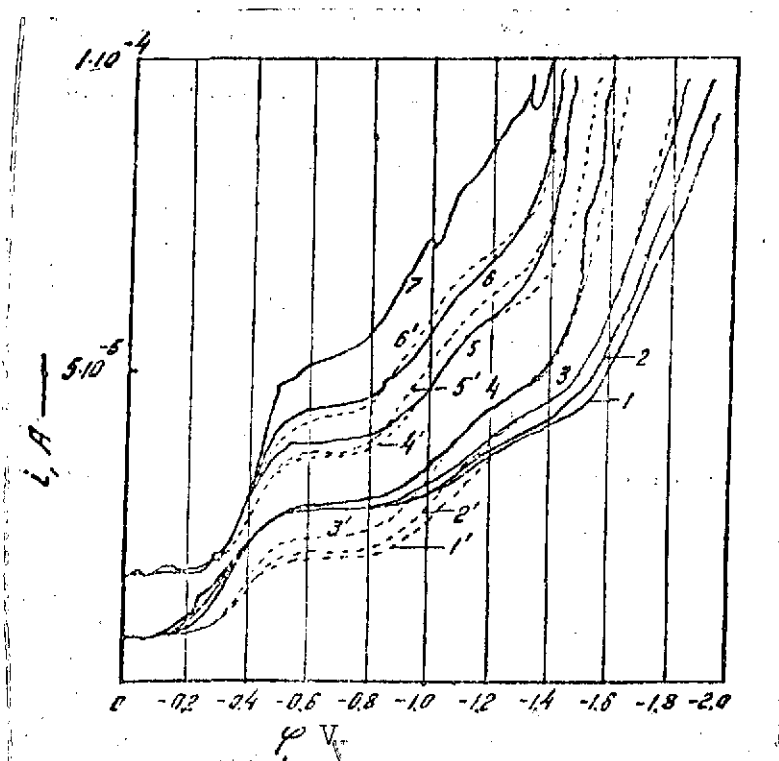


Fig. 8. Polarograms of Cr (II)-Cr (III) oxidation-reduction in 0.1 M Na_2SO_4 solution, pH 2.3, shunt 1/500. Temperature: 1, 1'. 20° ; 2, 2'. 25° ; 3, 3'. 30° ; 4, 4'. 40° ; 5, 5'. 50° ; 6, 6'. 60° ; 7. 80° . Polarograms 1-7 were taken in sequence, during heating of the solutions from 20 to 80° . Polarograms 7'-1' were taken during cooling of the same solutions.

The dependence of the anode and cathode half-wave potentials is presented in Fig. 11 for normal and heated solutions. The change

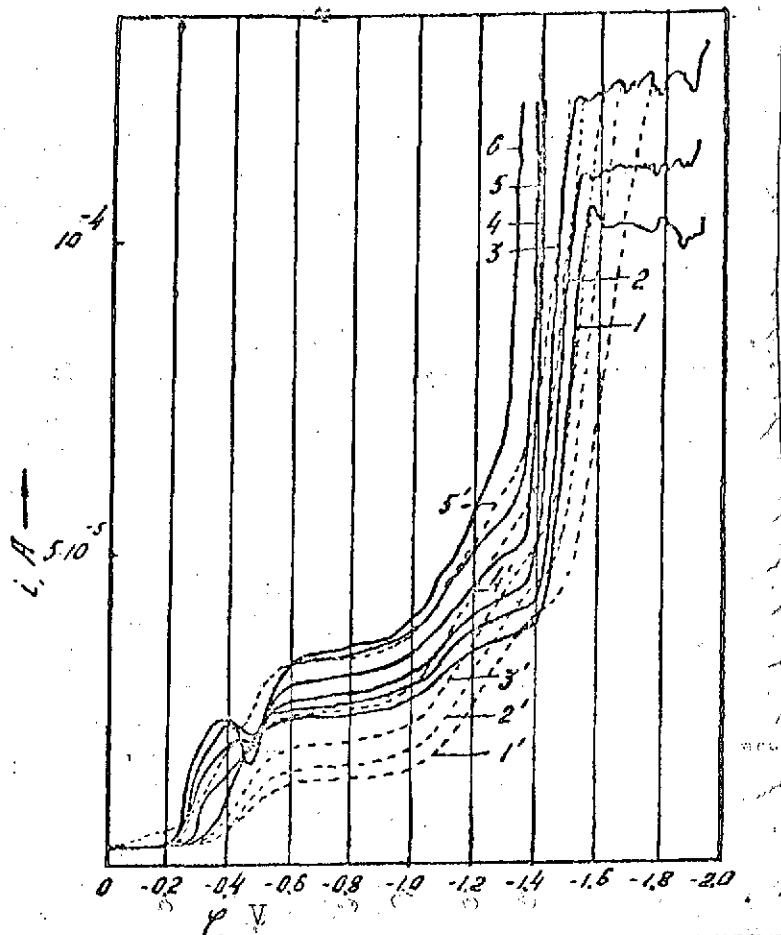


Fig. 9. Polarograms of Cr (II)-Cr (III) oxidation-reduction in 0.1 M Na_2SO_4 solution, pH 2.9, shunt 1/300. Temperature: 1,1'. 20°, 2,2'. 30°; 3,3'. 40°; 4,4'. 50°; 5,5'. 60°; 6. 80°. Polarograms 1-6 were taken in sequence, during heating of the solutions from 20 to 80°. Polarograms 6-1' were taken during cooling of the same solutions.

in exchange current density for the Cr (III) (III) \rightleftharpoons Cr (II) reaction vs. temperature is shown in Fig. 12.

For solutions with pH from 1.6 to 2.9, two irreversible waves are found on the polarograms (concerning the Cr (III) \rightleftharpoons Cr (II) reaction). One is the Cr (II) oxidation wave and the other is the Cr (III) reduction to Cr (II). With increase in temperature, the anode wave half-wave potentials are shifted in the more negative direction and the cathode, in the more positive, in this manner approximating the equilibrium half-wave potentials (Fig. 8). /60

For solutions with pH 2.9 and higher, in addition to the Cr (II)-Cr (III) oxidation-reduction waves, a third wave is observed on the polarogram, corresponding to reduction of the chromium ions to the metal.

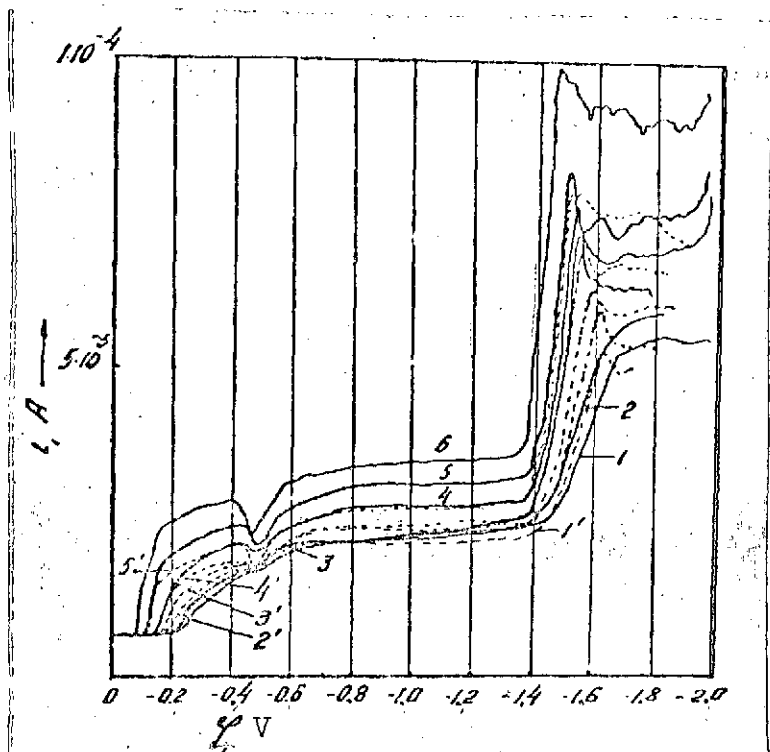


Fig. 10. Polarograms of Cr (II)-Cr (III) oxidation-reduction in 0.1 M Na_2SO_4 solution, pH 3.8, shunt 1/300. Temperature: 1,1'. 20°; 2,2'. 30°; 3,3'. 40°; 4,4'. 50°; 5,5'. 60°; 6. 80°. Polarograms 1-6 were taken in sequence, during heating of the solutions from 20 to 80°. Polarograms 6-1' were taken during cooling of the same solutions.

On polarograms of solutions with pH above 2.9 and temperatures above 40° (Figs. 9, 10), the anode Cr (II) oxidation wave is split into two. In this case, the initial section of the oxidation wave remains in the former location, but the second oxidation wave formed is shifted in the positive direction. With increase in temperature and pH of the solution, the height of the new wave increases, at the expense of reduction in height

of the preceding oxidation wave. This circumstance evidently is connected with the fact that, under these conditions, poorly soluble hydroxy salts of trivalent chromium can form in the electrode layer, blocking the anode.

It is seen from Figs. 8-12 that the half-wave potentials and the Cr (III) \rightleftharpoons Cr (II) reaction exchange currents, at the same temperature, especially at 20°, are not uniform, and that they depend on whether the polarograms were taken immediately after preparation of the solutions at 20° or whether they were heated to 80° and again cooled to 20°. It is interesting to note

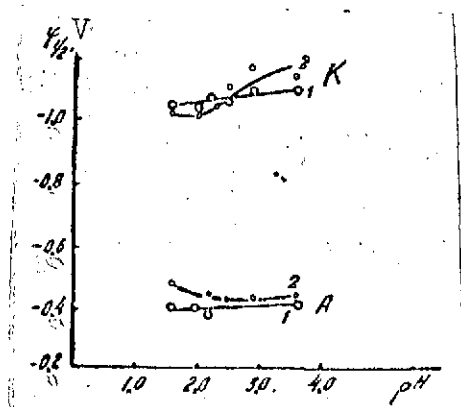


Fig. 11. Cr (III)-Cr (II) half-wave potentials vs. solution pH in 0.1 M Na_2SO_4 , t 20°; K for cathode waves; A for anode waves; 1 for initially prepared solutions; 2 for heat treated solutions.

(see Fig. 11) that the oxidation and reduction half-wave potentials, for solutions with pH below 2.3 and 2.5, subjected to heating, became more reversible and, for solutions with pH above 2.5 less reversible, compared with the half-wave potentials of the initially prepared solutions.

An additional test of the effect of time of the temperature treatment and subsequent stabilization of the solutions, from 1 hour to 1 day, demonstrated complete identity of the results for various holding times. /62

The facts described above can be explained in the following manner. It is evident that, in the initially prepared Cr (III)-Cr (II) solutions, the trivalent chromium ion is present, not only in the form of hydrated and sulfate complexes, occurring in equilibrium for given ratios, but partially in the form of some more stable complex compounds. These more stable and non-labile compounds could be binuclear chromium complexes, which, according to some data in the literature, form to one degree or another in oxidation of divalent chromium ions by the oxygen in the air. Undoubtedly, their content in the solutions which we prepared may be very insignificant, since all measures were maintained, to eliminate the possibility of contact of the solutions with air, in preparation and storage of the solutions and in polarography of them. After heat treatment, the binuclear complexes apparently are destroyed.

In sufficiently acid solutions, in which the hydroxo complexes are not stable, after destruction of the binuclear chromium

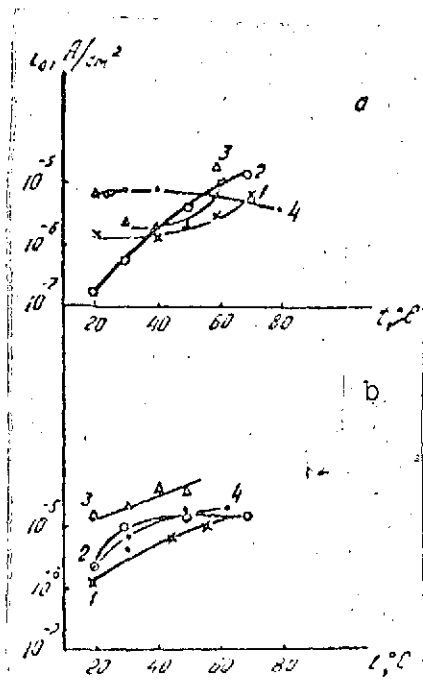


Fig. 12. $\text{Cr (III)} \rightleftharpoons \text{Cr (II)}$ reaction exchange current density in 0.1 M Na_2SO_4 solution vs. temperature: a. for heated solutions; b. for cooled solutions; pH: 1. 1.6; 2. 2.0; 3. 3.2; 4. 2.3.

complexes by heat treatment, the chromium ions remain bound only to water molecules and sulfate anions.

At low temperature and low SO_4^{2-} concentration (0.1 M and less), the predominant complexes in the solution under equilibrium conditions apparently are the violet trivalent chromium hexahydrates, which are most stable in sulfate solutions. And, since equilibrium is established very rapidly between the sulfate and hydrate Cr (III) complexes, in the presence of divalent chromium ions [21], the half-wave potentials on the polarographs of the solutions after heat treatment are shifted towards less polarization.

With decrease in acidity of the initially prepared solutions, the possibility arises of formation of mixed sulfate-hydroxo complexes, OH and oxo compounds, the transition to which is greatly slowed, however. An increase in temperature evidently accelerates these processes and, therefore, as a result of the thermal treatment, the concentrations of the more stable complexes in the solution increases. This appears on the polarograms, as a shift in the half-wave potentials (especially of the cathode wave) towards an increase in irreversibility of the processes.

Fig. 12 a and b represents the dependence of the exchange currents of the $\text{Cr (III)} \rightleftharpoons \text{Cr (II)}$ reaction in 0.1 M Na_2SO_4 on temperature, for solutions subjected to heating and subsequent

cooling. In the first case (Fig. 12 a), a great spread of points is noticed, and, in the second case (Fig. 12 b), a tendency is clearly seen towards delay in growth of the oxidation-reduction reaction exchange currents with increase in temperature above 40°.

This nature of the dependence of exchange currents on temperature confirms the conclusion that preliminary heating of Cr (III)-Cr(II) solutions accelerates establishment of equilibrium conditions in them.

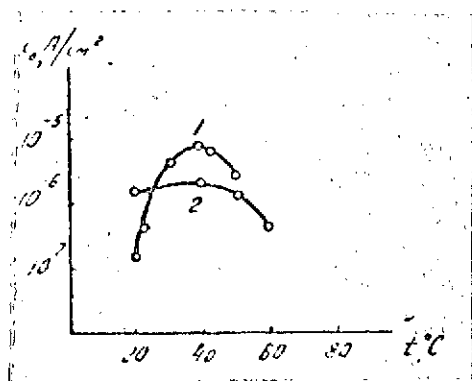


Fig. 13. Cr (III) \rightleftharpoons Cr (II) reaction exchange current density in 0.01 M Na_2SO_4 solution vs. temperature: 1. for heating solutions; 2. for cooling solutions.

Since the lag in increase in Cr (III)-Cr (II) reaction exchange currents with increase in temperature was caused by change in equilibrium composition of the Cr (III) complexes with temperature, namely, by conversion of the hydro-complexes predominating in the solution at low temperature to the more stable sulfate complexes at increased temperatures, the observed effect may increase with decrease in concentration of the SO_4^{2-} background, since the equilibrium fraction of trivalent chromium bound to the sulfate anion at low

temperatures decreases still more with decrease in sulfate anion concentration.

The results of Cr (III) \rightleftharpoons Cr (II) reaction exchange currents vs. temperature, concerning more dilute SO_4^{2-} solutions (down to 0.01 M), are presented in Fig. 13.

Not only a drop in growth of exchange currents with increase in temperature, but a decrease in them at temperatures above 40°, are clearly expressed here.

Conclusions

1. The electrochemical behavior of Cr (III)-Cr (II) was studied, in a mercury drop electrode in sulfate solutions.
2. The transport numbers, Cr (II) \rightarrow Cr (III) oxidation-reduction reaction exchange currents, composition and apparent instability constants of the Cr (III) sulfate complexes formed, were determined.
3. For the case of Cr (II)-Cr (III) ion reduction-oxidation, in dilute sulfate solutions (0.1 M) and below), an unusual temperature dependence of the reaction exchange currents was found, passing through a maximum, which is explained by change in composition of the Cr (III) complexes in the solution, and which confirms the observations of A.V. Pamfilov and colleagues, of change in certain properties of chromium salt solutions, with transition of the solution temperature through 40-50°.

REFERENCES

1. Grinberg, A.A., Vvedeniye v khimiyu kompleksnykh soedineniy [Introduction to the Chemistry of Complex Compounds], Moscow-Leningrad, "Khimiya" Press, 1966.
2. Pamfilov, A.V. and Puchkova, N.N., Zh. Obshch. Khim. 26(4), 955 (1956).
3. Pamfilov, A.V., Lopushinskaya, A.I., and Balter, A.M., Zh. Fiz. Khim. 36(11), 2481 (1962). /64
4. Pamfilov, A.V., Lopushinskaya, A.P., and Balter, A.M., Zh. Fiz. Khim. 37(3), 615 (1963).
5. Pamfilov, A.V., Lopushinskaya, A.I., and Belaya, A.M., Ukr. Khim. Zh. 30(2), 173 (1964).
6. Lopushinskaya, A.I., Pamfilov, A.V. and Tsisar', I.A., Ukr. Khim. Zh. 30(8), 777 (1964).
7. Soo', A., Giurgiu, U., and Cadariu, J., Studio. Univ. Rades - Bolyai Ser. Chem. 8(2), 61 (1963); RZhKhim 1(4), 8118 (1966).
8. Emerson, K., and Sragen, N.M., J. Inorg. and Nucl. Chem. 11(4), 309 (1959).
9. Nisikhara Kiënado, Kurati Mistsyo, and Nisin Khrosi, Trans. Mining and Metallurg. Alumini Assoc. 15(4), 203 (1964); RZhKhim 236, 795 (1964).
10. Rollinson, K., in the collection Khimiya koordinatsionnykh soedineniy [Chemistry of Coordination Compounds], D.M. Beylar, Jr. (ed.), Moscow, "IL" Press, 1960, p. 379.
11. Beylar, D.M., and Bush, D., Tetrahedron, p. 8.
12. Ardon, M. and Linenberg, A., J. Phys. Chem. 65(8), 1143 (1961).
13. Geyrovskiy, Ya., and Kuta, Ya., Osnovy polyarografii [Principles of Polarography], Moscow, "Mir" Press, 1965.
14. Stromberg, A.G., Zh. Fiz. Khim. 27, 1287 (1953).
15. Stromberg, A.G., Zh. Fiz. Khim. 29, 63, 409 (1955).
16. Stromberg, A.G., in the collection Teoriya i praktika polyarograficheskogo analiza [Theory and Practice of Polarographic Analysis], Kishinev, "Istiintsa" Press, 1962, p. 177.

17. Stromberg, A.G. and Kartushinskaya, A.I., Zh. Fiz. Khim. 35(5), 1058 (1961).
18. Stromberg, A.G. and Igolinskiy, V.G., Zh. Fiz. Khim. 36(12), 2714 (1962).
19. Vasil'yeva, Ye.I., Zabotin, P.I., and Kir'yakov, G.Z., in the collection Elektrodnyye protsessy na tverdykh i zhidkikh elektrodakh [Electrode Processes in Solid and Liquid Electrodes], Trudy In-ta Khim. Nauk AN KazSSSR, Vol. 12, 1964, p. 57.
20. Rozotti, F., in the collection Sovremennaya khimiya koordinatsionnykh soedineniy [Modern Chemistry of Coordination Compounds], D.I. Louisa and R. Wilkins (eds.), Moscow, "IL" Press, 1963, p. 13.
21. Kozlovskiy, M.T. and Zabotkin, P.I., Izv. AN KazSSR, Ser. Khim. 10, 40 (1956).